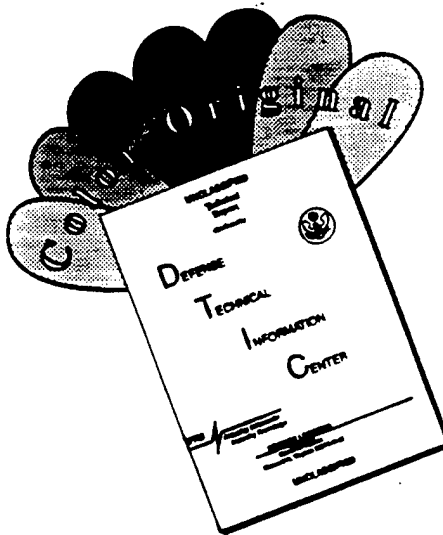


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# **A Portable Laser Induced Breakdown Spectrometer for Toxic Metals**

## **Phase I Final Report**

### **Abstract**

During the Phase I of this research project, a compact, portable laser induced breakdown spectroscopy (LIBS) instrument for the detection of Pb in soils and in paints has been designed and evaluated in the laboratory. Fundamental studies of the temporal, spatial and spectral evolution of the LIB plasma have made possible an improved optimization. The instrument consists of a very compact Nd:YAG laser, the Kigre Model MK-367, operating at 1 Hz with a 21 mJ output at 1064 nm. The laser produces a reliable, reproducible breakdown on all of the materials investigated (soils, painted surfaces, metals and in air). The design calls for the detection system to be based around the Ocean Optics S2000 series CCD array spectrometer which will not be available until early in December, 1996. Therefore, the evaluations were carried out using an ungated model S1000 spectrometer and a gated 0.5 m focal length laboratory spectrograph. While the S1000 spectrometer provides reasonable spectra, the signal to noise ratio is substantially degraded because this spectrometer cannot be gated to exclude intense background early in the plasma formation. It also provides relatively poor spectral resolution. Therefore, additional studies were also made with the larger 0.5 m focal length laboratory spectrometer, which is both gated and of resolution (0.08 nm) comparable to that of the S2000, using the Ocean Optics fiber optic input probe as the detection optic. With this system, a very conservative limit of detection for Pb in paint of 60  $\mu\text{g/g}$  was obtained for a single laser pulse, considerably better than what was originally anticipated. It is expected that the S2000 spectrometer will perform equally well. Therefore, the results of the Phase I studies indicate that the combination of the small Kigre Nd:YAG laser and the Ocean Optics S2000 spectrometer is a viable approach to a portable, sensitive LIBS instrument.

## Overview of Phase I Studies

Much of the results from the Phase I research have been reviewed in the Phase II proposal. These will not be duplicated in this report. The accomplishments, which include data obtained both before and since the Phase II proposal was prepared, are outlined as follows:

### *Temporal/spatial/spectral studies of the LIB plasma*

The temporal-spectral development of the LIB plasma was studied for the important Pb atomic and ionic lines for a plasma on pure lead and on a surface coated with paint containing Pb and in Pb contaminated soils. The spatial development was studied using a system which provided two temporally resolved orthogonal images of the plasma at several fixed wavelengths. From the studies, we conclude that:

1. The spatial development of the plasma is dependent upon the matrix. Plasmas formed on pure Pb were more cylindrical in shape with a significant atomic population at greater heights above the sample surface than for plasmas formed on soils and painted surfaces. Figure 1 shows orthogonal images of the total emission from plasmas formed on pure Pb, 10% Pb in paint and 25% Pb in soil. They represent a 15  $\mu$ s integration begun 1  $\mu$ s after the initiation of the breakdown.
2. Regardless of the matrix, the plasma begins to develop along a preferential axis coinciding with the incident laser beam.
3. The plasma shape is dependent upon the angle of incidence of the laser beam with respect to the surface.

4. The principal plasma spatial expansion is during the first 500 ns when it is emitting only continuous background.
5. As the emission of atomic and ionic lines becomes prominent, the expansion process stops, the continuum background decreases and the plasma begins to decay.
6. The ionic line intensity decays much faster than the atomic line emission intensity.
7. The optimum angle of observation depends upon the matrix. For pure Pb samples, the optimum viewing angle was  $0^\circ$  with respect to the incident beam, for soils the optimum was close to  $45^\circ$  and for the painted surfaces about  $80^\circ$  (nearly perpendicular to the incident beam).
8. In studies on paint and soil samples, for a 20 mm focal length lens on the Kigre Nd:YAG laser, the plasma shape and intensity did not vary significantly within  $\pm 2$  mm of the beam focus. Figure 2 shows orthogonal spectral images of the plasma formed on a soil sample. The elongated structures which appear at focusing distances of +2 and +3 mm are caused by the breakdown of the laser above the surface of the sample.

#### *Evaluation of the LIB spectrum of Lead*

To aid in the identification of suitable spectral lines and to find potential spectral interferences, a complete temporally resolved spectrum of Pb was obtained from pure Pb and from Pb contaminated

soil. A total of 34 useful atomic and ionic lines were identified, the weakest being about 20X weaker than the most intense line. The most intense line was the 280.1995 nm atomic line; the 405.7807 nm transition was only about 30% less intense. The 280.1995 nm line is often interfered with by a Mg ion line at 280.27 nm, especially in soils. Therefore we have used the 261.4175 nm Pb line which is generally well isolated and only 6% less intense. Both the 261 nm and the 406 nm lines can be resolved with a spectral resolution of 0.08 nm in the spectra that were observed from Pb contaminated paints and soils.

#### *Confirmation of the Feasibility of the Ocean Optics Spectrometer for LIB Detection*

A Model S1000 Ocean Optics spectrometer was available for the Phase I studies. It has a spectral resolution of only 0.8 nm and cannot be gated. Our unit had a spectral coverage from 230 - 300 nm. Optical coupling was made with a fiber optic link (single 200  $\mu$ m fiber) from the entrance slit to a probe containing a 2.5 cm focal length lens (f/3 collection). The Ocean Optics Model S2000, which will be available early in December, 1996, will replace the S1000 in further studies. It can be gated with a 10  $\mu$ s resolution, has 0.08 nm spectral resolution (10X better) than the S1000 and a higher quantum efficiency CCD detector.

Using the S1000 system, spectra were obtained from pure Pb samples, Pb containing paint and Pb contaminated soils. For example, Figure 3 shows spectra taken of pure Pb and Pb contaminated soil. A calibration curve was constructed from standard Pb paint samples using the 261 nm transition and the Kigre laser. It is shown in Figure 4. These signals were obtained by integrating over an accumulated 20 s time window during which the laser was fired 10 times. Therefore, the Pb emission lines sit on a large accumulated dark count as well as the total background emission of the

plasma, often containing only background continuum. This accounts for the relatively poor (30%) standard deviation. Nevertheless, a 2% concentration of Pb was easily detected.

### *Confirmation of the Feasibility of the Kigre MK-367 Laser for LIBS*

Most of our earlier fundamental studies were carried out using a 150-200 mJ, 14 ns, 30 Hz Nd:YAG laser. One goal of our Phase I studies was to prove that the very small Kigre Model MK-367 laser was capable of producing a reliable LIB plasma of useful intensity. The Kigre laser produces 21 mJ pulse energy in a duration of about 5 ns and therefore has a peak power density of about a factor of three lower than the larger laser which was previously used. The unit which we evaluated was uncooled and therefore capable of a maximum repetition rate of 0.3 Hz.

These studies were made using a 0.5 m focal length spectrograph fitted with a gated CCD detector. This system has the same spectral resolution (0.08 nm) as the S2000 Ocean Optics spectrometer and somewhat poorer light gathering power. The Ocean Optics fiber optic input probe was used to collect light from the plasma and deliver it to the entrance slit of the spectrometer. Figure 5 shows *single shot* spectra obtained for samples of pure Pb, 0.5% Pb in paint and blank paint. The spectra have been offset for clarity but have nearly equivalent background levels. Note that a small Pb line can even be detected in our blank paint. A linear calibration function was obtained for Pb levels below about 1%, as shown in Figures 6 and 7. The non-linear response shown in Figure 6 at concentrations above 1% is expected considering the ca. 10 ng of sample which is ablated by the laser into a plasma volume of ca.  $0.001 \text{ cm}^3$ . For a 1% Pb sample, this corresponds to a Pb number density of the order of  $3 \times 10^{14} \text{ cm}^{-3}$  which is in the region in which self-absorption is expected to occur in emission. Figure 7 shows a plot of the points in the linear region below 1% Pb. Based on

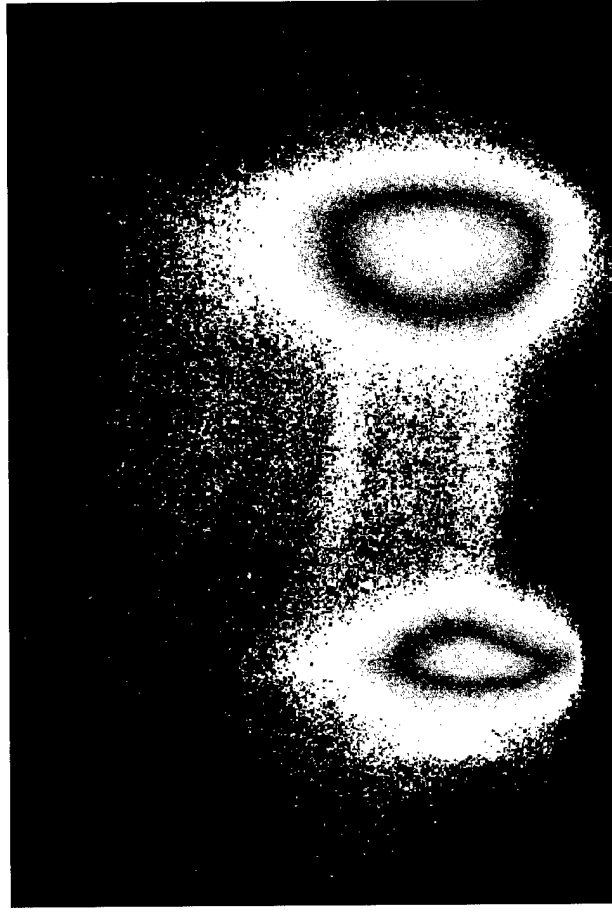


the peak areas and the background noise in a single laser shot, the estimate for the limit of detection based on this measurement to be 60 ppm. This is calculated for a single laser shot.

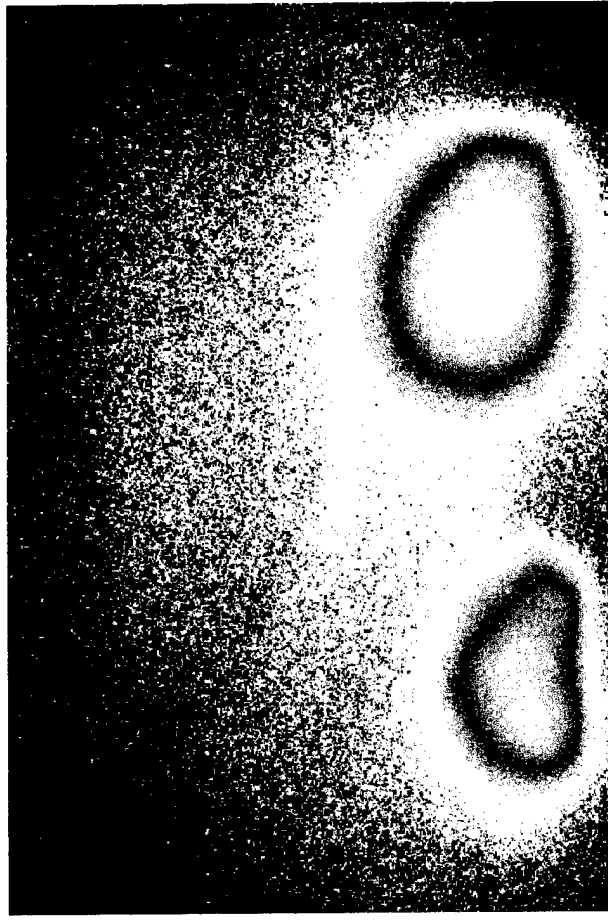
A spectrum was also obtained for Pb in reference Montana soil with this system. Figure 8 shows the result, for a *single laser shot*, for a soil sample containing 1162 ppm Pb. The S/N for the 406 nm Pb line is quite good. In addition, several other lines can be identified in the same spectral window. Strontium, for example, is present at a concentration of about 245 ppm, manganese at 638 ppm, iron at 2.89%.

Based upon these results, we conclude that the combination of the Kigre MK-367 laser with an Ocean Optics S2000 spectrometer will provide a flexible, reliable, portable, sensitive LIBS system for multielement detection in soils and painted surfaces.

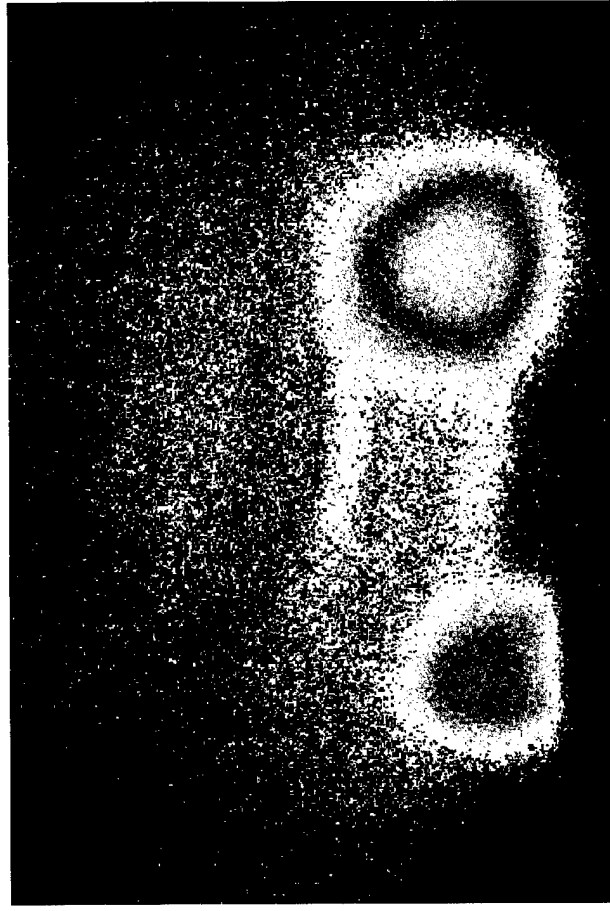
Figure 1



Pure Lead



10 % Pb in Paint



25 % Pb in Soil

Figure 2

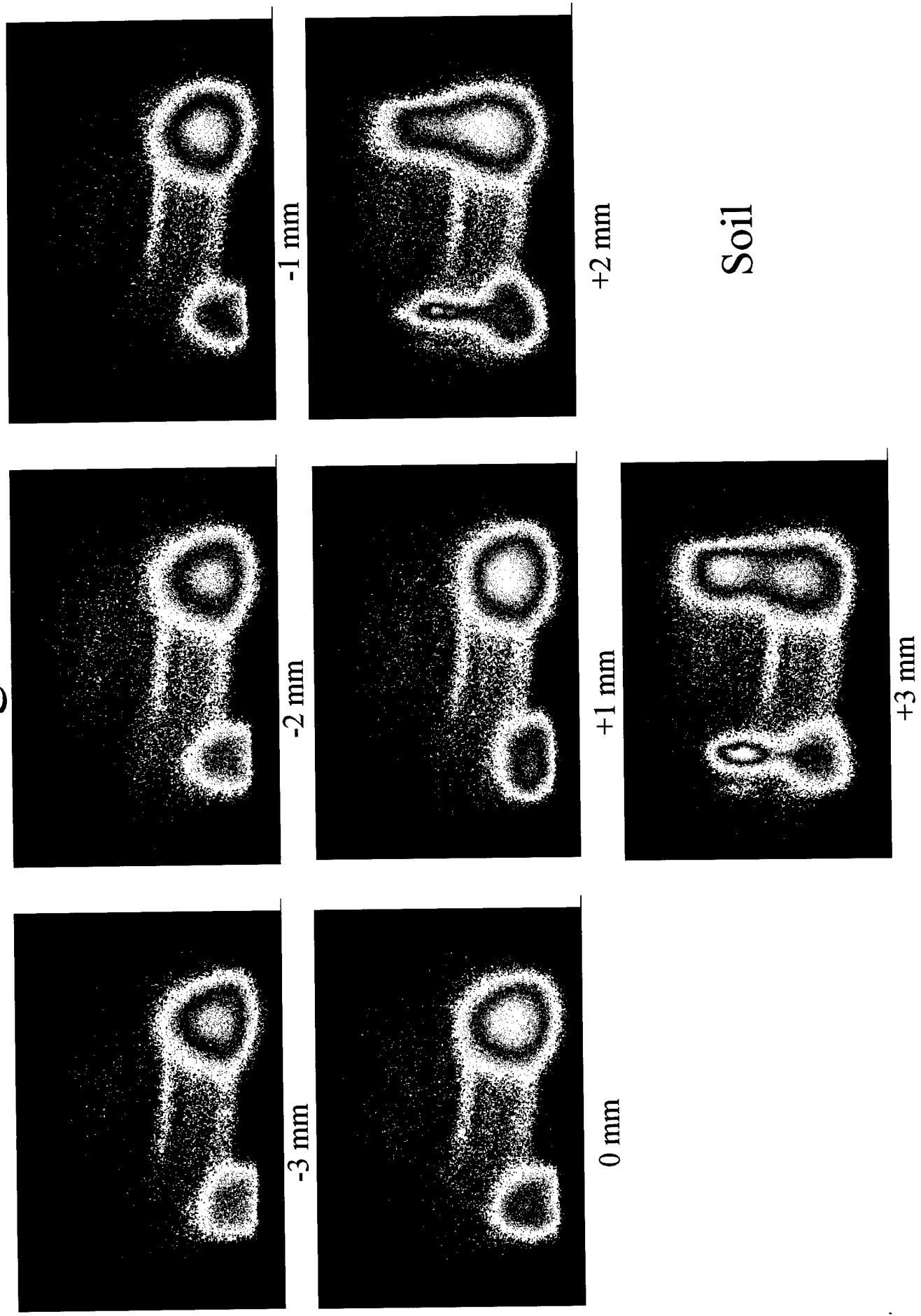


Figure 3

## Comparative Lead Spectrum

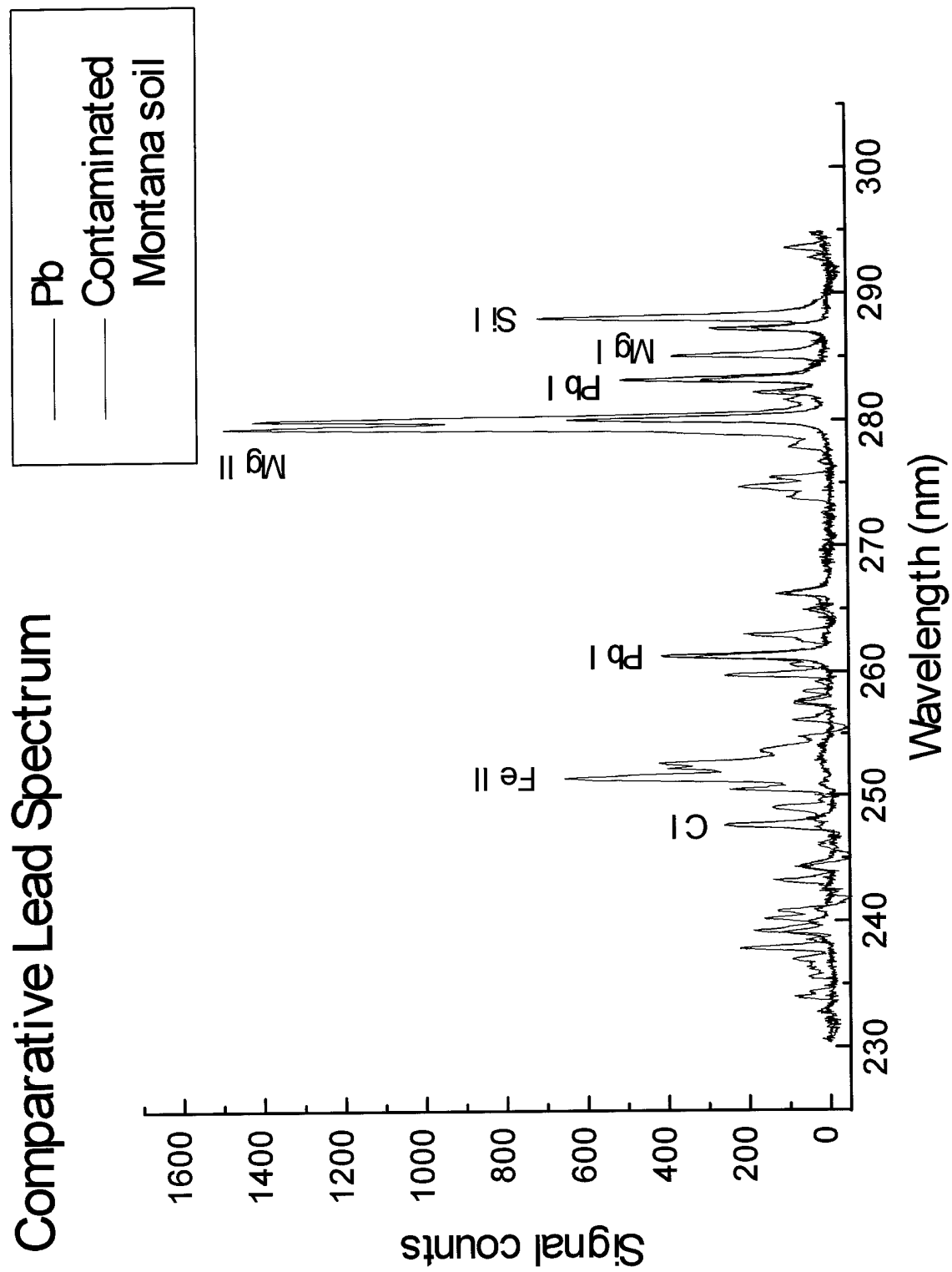


Figure 4

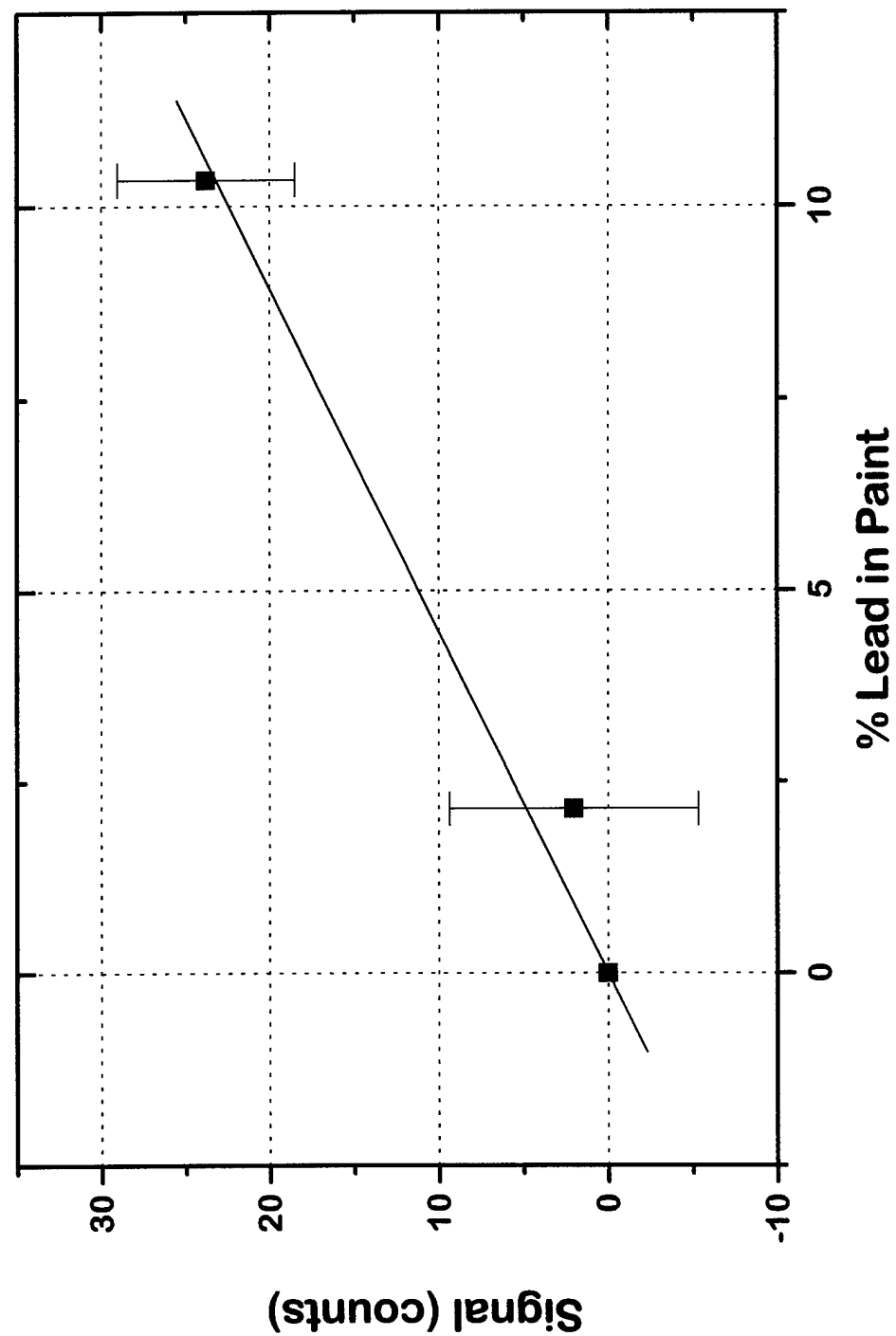


Figure 5

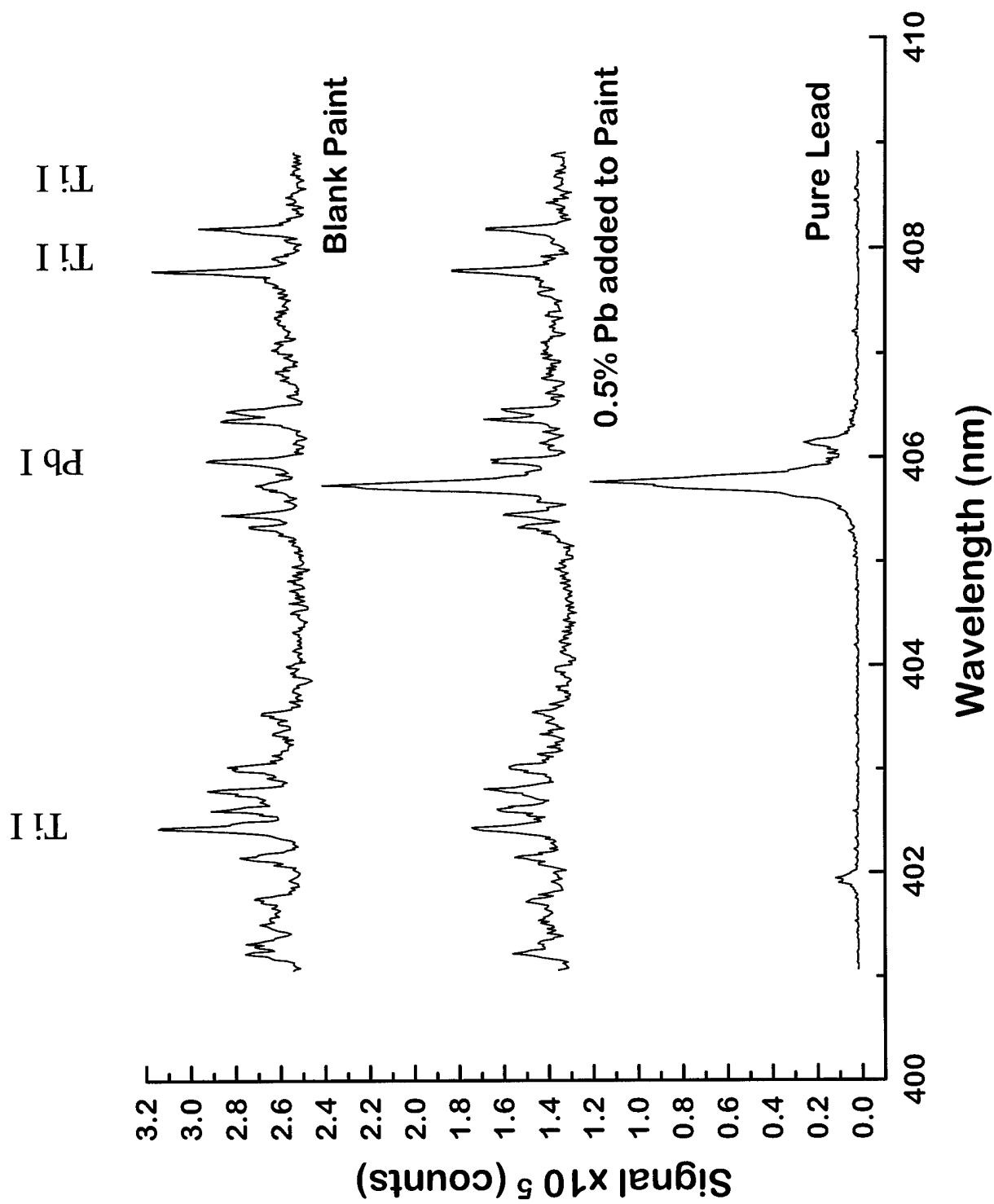


Figure 6

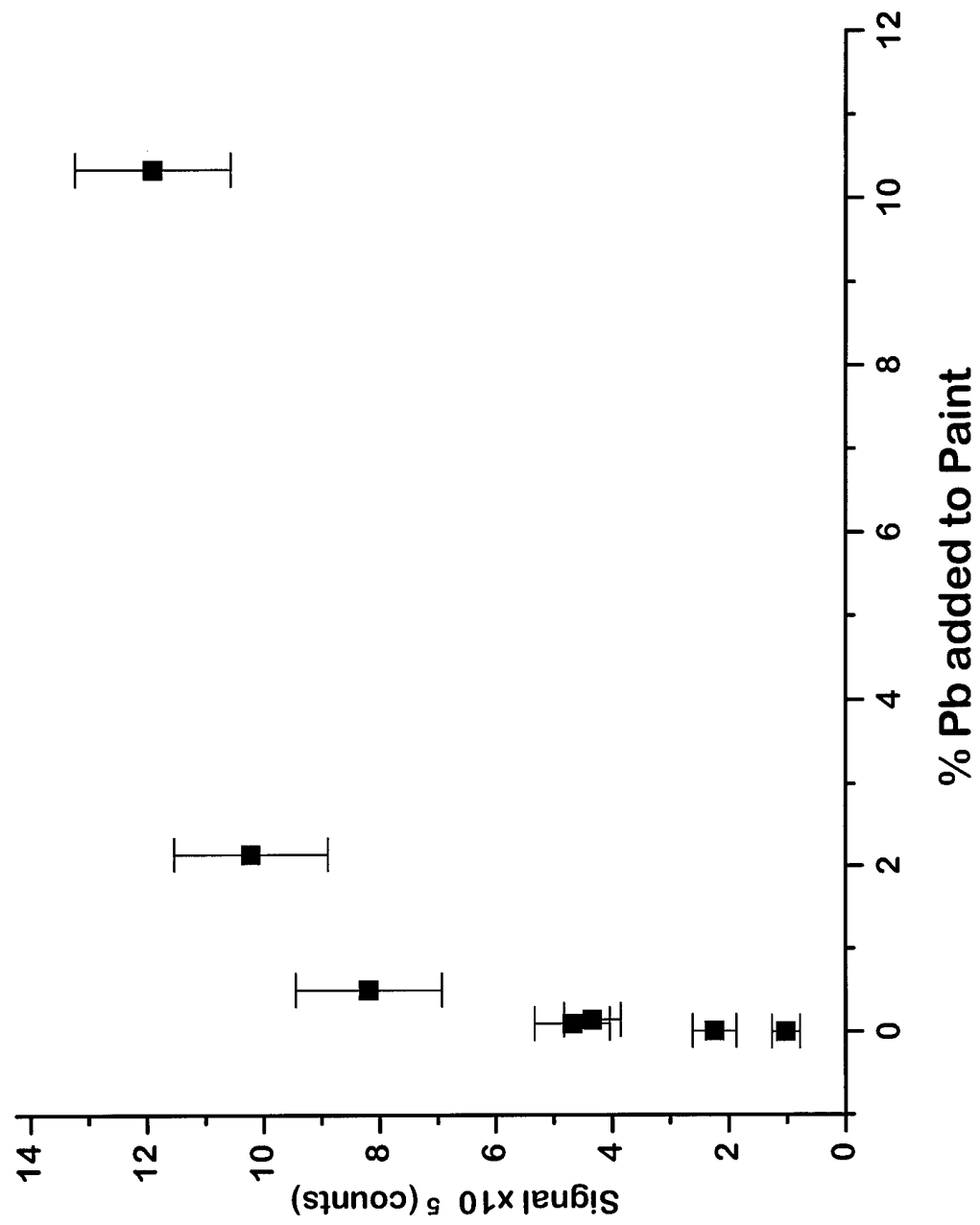


Figure 7

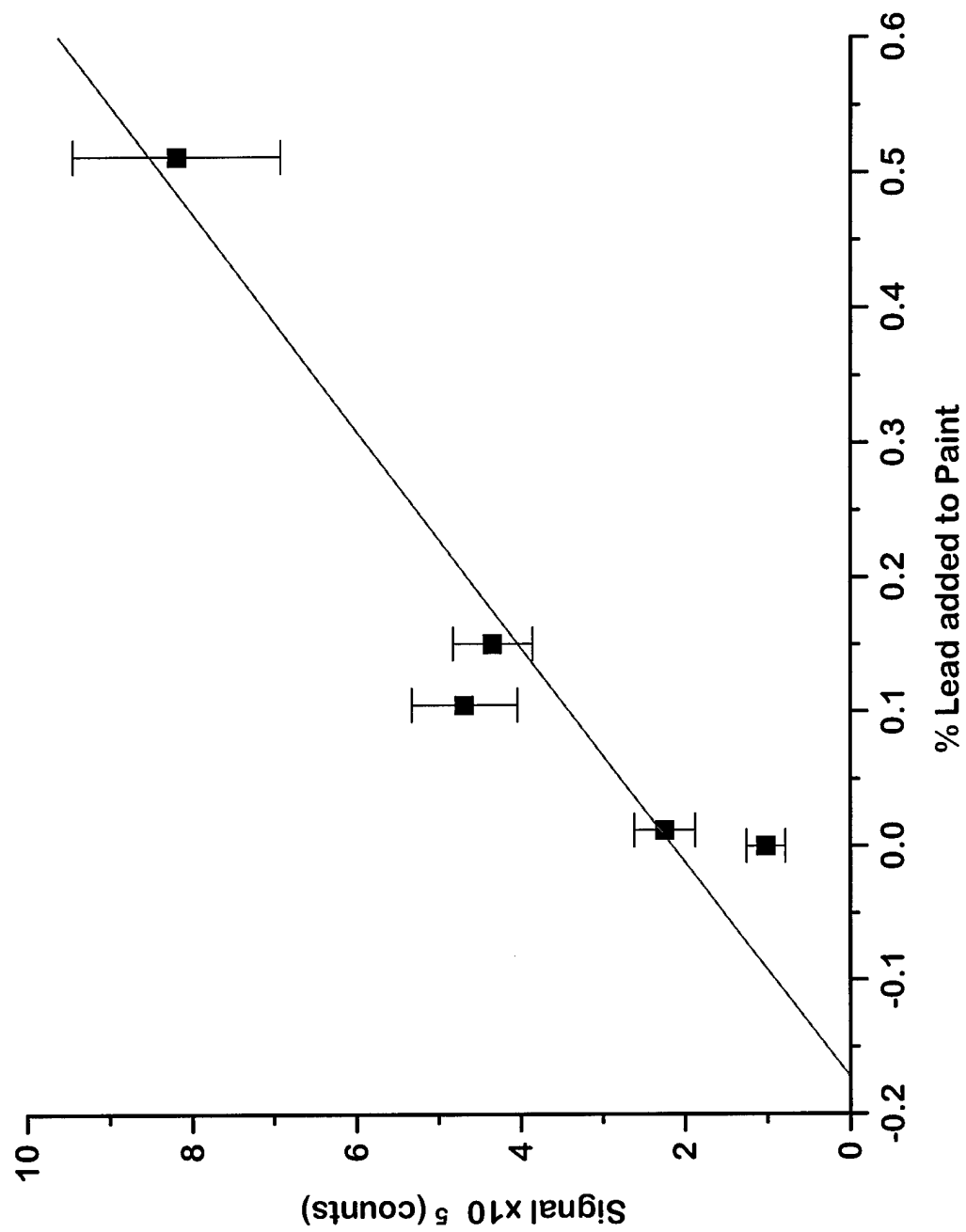




Figure 8

